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**THE CHARACTERISTICS OF ORGANIC MATTER FROM THE TRIASSIC
CLAYS OF NW MARGIN OF THE HOLY CROSS MTS (POLAND) –
PRELIMINARY REPORT**

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Abstract. The molecular character of organic matter in Triassic clays on the NW border of the Holy Cross Mts was determined in apolar, aromatic and polar fractions of extractable organic matter (OM) using GC-MS analysis. The contribution of terrestrial higher plants to the kerogene is revealed by the dominant presence of odd long-chain *n*-alkanes and by the occurrence of retene. Benzophenone, fluorenone, cyclopenta(*def*)phenanthrenone, antracenone and benzanthrone were among the compounds identified in polar fractions of the soluble organic matter. These commonly originate during strong oxidation of sedimentary organic matter. The aromatic fraction is characterised by the presence of phenyl derivatives (PhPAC) such as phenylnaphthalenes, terphenyls, phenyldibenzofurans and phenylphenanthrenes that are also products of the abiotic oxidation of organic matter. The oxidation processes that occurred during sedimentation and during early diagenesis resulted in a very significant decrease in the organic matter content in the clays. This decrease considerably influences their technological properties.

Key-words: Triassic clays, the Holy Cross Mts, organic matter, biomarkers, maturity

INTRODUCTION

The problem of organic matter in clay raw materials used by the ceramic industry has been one of great importance over recent years. It has arisen due to the introduction of the fast firing technology, now commonly used in the production of ceramic tiles. It is assumed that the organic matter in raw material for wall and paving tiles produced in a single fast firing, expressed as elemental carbon, should be lower than 0.3 wt.% (de la Torre et al. 1996). Otherwise, production defects can appear resulting, among others,

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from excessive organic matter contents (Beltrán et al. 1988). The characteristics of this organic matter and its content in clay rocks are of both cognitive and industrial importance. The former aspect is a main goal of this paper.

To-date, the literature concerning Polish clay rocks and clay raw materials contains few reports on organic matter occurring in elevated amounts. Total organic matter (TOC) in the kaolin from the Kalno (Lower Silesia) deposit amounts to approx. 1.5 wt.% (Sikora et al. 1978). Some Jurassic clays are characterised by TOC in the range 0.4–3.0 wt.% (Zatoń, Marynowski 2004, 2006; Marynowski et al. — in preparation).

Cognitive and practical aspects are the basis for initiating the current study on the organic matter contents of clay rocks that are of considerable economic importance even if their organic matter content is distinctly lower than in the clays mentioned above. The Triassic red clays of the NW border of the Holy Cross Mts are examples of such rocks. The organic matter occurring in these clays has not, as yet, been characterized in compositional terms either quantitatively or qualitatively. One of the reasons for this is the negligible amount of organic matter in these rocks which inhibits the application of, e.g., thermal analysis. Complex analytical procedures are required to extract the organic matter from the clays as are precise chromatographic and spectroscopic analytical methods.

This paper presents data on the general character of the organic matter in the Triassic red clays (samples: Chełsty 444, Baranów 947, Kozów 873) and in grey and green lenses and intercalations (samples: Chełsty 449, Kozów 869). The molecular composition of extractable organic matter has been analysed for those organic compounds (including biomarkers) that characterize the source of this matter and the level of its thermal maturity.

SAMPLES AND METHODS

Clay samples were collected from three operating open pits at Chełsty (Keuper), Kozów (Buntsandstein) and Baranów (Buntsandstein), all on the NW border of the Holy Cross Mts (Fig. 1). Total organic carbon (TOC) was determined by the LECO method using a CR-12 apparatus.

Extraction and fractionation. Samples were Soxhlet-extracted in pre-extracted thimbles with dichloromethane. The extracts were separated using pre-washed TLC plates coated with silica gel (Merck, 20 × 10 × 0.25 cm). Prior to separation, the TLC plates were activated at 120°C for 1 h. The plates were loaded with the *n*-hexane soluble fraction and developed with *n*-hexane/dichloromethane (V:V = 97:3). Bands comprising aliphatic (R_f 0.5–1.0), aromatic (R_f 0.05–0.5) and polar + asphaltenes (R_f 0.0–0.05) fractions were collected.

In addition, polar fractions were further developed with *n*-hexane/ethyl acetate (V:V = 9:1) on TLC plates coated with silanised silica gel (Merck, 20 × 20 × 0.25 cm). Three subfractions were obtained by this means. Polar oxygen compounds characterized the second subfraction (R_f = 0.5–0.8). This latter, and the aliphatic and aromatic fractions were analysed in further detail.

Gas chromatography coupled with mass spectrometry (GC-MS). The analyses were performed using an Agilent 6890 Series Gas Chromatograph interfaced with an Agilent

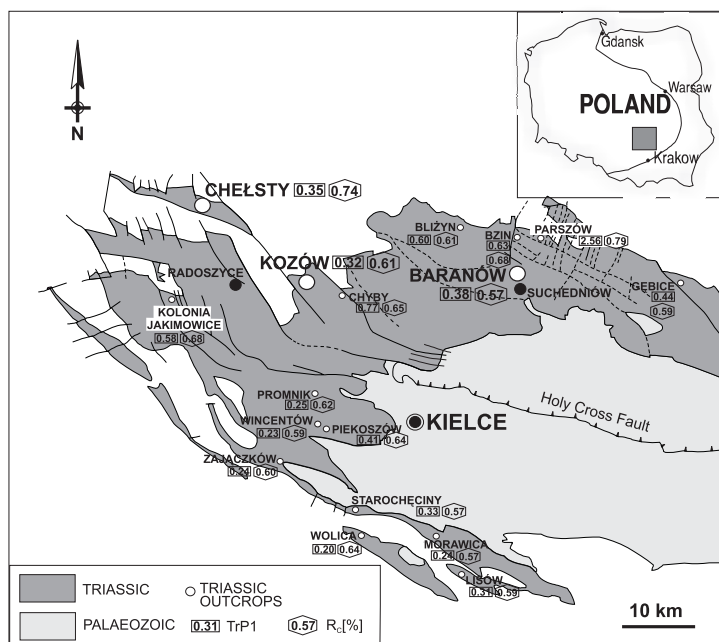


Fig. 1. Location map of the Holy Cross Mts and their northern Triassic cover.
 TrP1 — terphenyl ratio parameter (increases with increasing maturity),
 Rc — calculated vitrinite reflectance value based on MPI1 (see Table 1)

5973 Network Mass Selective Detector with an Agilent 7683 Series Injector (Agilent Technologies, Palo Alto, CA). An Agilent Technologies Enhanced ChemStation G1701CA ver.C.00.00 was used for the data collection and the Wiley Registry of Mass Spectral Data 7th Edition software for the mass spectra processing. 0.5 µl of sample was injected into a cool on-column injector with electronic pressure control, the temperature of which, in “Track Oven” mode, was 3°C higher than that of the oven.

Helium 6.0 (Linde, Kraków) at a constant flow rate of 2.6 ml/min. was used as the carrier gas. Analysed compounds were separated on a two fused-silica capillary columns: J&W DB5-MS (60 m × 0.25 mm i.d., 0.25 µm film thickness) and DB35-MS (60 m × 0.25 mm i.d., 0.25 µm film thickness).

The GC oven temperature was programmed from 40°C (isothermal for 1 min) to 120°C at a rate of 20°C/min and then to 300°C at a rate of 3°C/min. The final temperature was held for 35 min. The GC column outlet was connected directly to the ion source of the mass spectrometer. The GC-MS interface was held at 280°C and the ion source and the quadrupole analyzer at 230°C and 150°C, respectively. Mass spectra were recorded at m/z 45–550 (0–40 min) and m/z 50–700 (above 40 min). The mass spectrometer operated in the electron impact mode (ionization energy: 70 eV).

Differential Thermal Analysis. DTA analyses were carried out using a DERIVATOGRAPH-C apparatus of Hungarian production. The analytical conditions were as follows: temperature range 25–1000°C, heating rate 10 deg·min⁻¹, atmospheric air, referring substance Al₂O₃, Pt crucibles.

BULK GEOCHEMICAL DATA

Total organic carbon (TOC) in the material studied is very low being in the range 0.05–0.14 wt.% (Table 1). The presented data correspond to extractable organic matter contents (EOM — Table 1) which are also very low, at *ca* 0.01%. These observations concur with the results of thermal analysis (Fig. 2); the DTA curves do not show the diffused exothermic effect of organic matter combustion that is usually recorded between 350 and 500°C. The DTA detection limit for organic matter amounts to 0.2 wt.% (Łuczak-Wilamowska, Wyrwicki 2000).

TABLE 1

Selected biomarker characteristics of organic matter in red and green clays from the Holy Cross Mts

Sample	TOC [%]	EOM [%]	Al [%]	Ar [%]	Pol+Asph [%]	CPI ₍₂₅₋₃₁₎	Pr/Ph	Pr/ <i>n</i> C ₁₇	Ph/ <i>n</i> C ₁₈	MPI1	Rc [%]	TrP1	3-MeP/ Ret
Chelsty 444	0.14	0.012	34	7	59	0.91	0.95	0.54	0.57	0.57	0.74	0.35	2.68
Chelsty 449	0.07	0.011	34	11	55	0.99	0.98	0.84	0.98	0.16	0.50	0.39	1.64
Baranów 947	0.05	0.006	29	5	66	1.19	0.86	0.61	0.57	0.28	0.57	0.38	3.13
Kozów 869	0.06	0.008	71	12	17	1.03	0.56	0.85	0.73	0.35	0.61	0.32	2.61
Kozów 873	0.11	0.009	54	10	36	1.05	0.71	0.96	0.76	0.31	0.59	0.34	2.57

EOM — extracatable organic matter, **Al** — aliphatic fraction, **Ar** — aromatic fraction, **Pol + Asph** — polar fraction and asphaltenes, **CPI₍₂₅₋₃₁₎** — carbon preference index for C₂₅ to C₃₁ *n*-alkanes range, **Pr/Ph** — pristane/phytane ratio, **Pr/C₁₇** — pristane/*n*-heptadecane ratio, **Ph/C₁₈** — phytane/*n*-octadecane ratio, **MPI1** — methylphenanthrene index 1, $MPI1 = 1.5([2-MP] + [3-MP])/([P] + [1-MP] + [9-MP])$ (Radke, Welte 1983), **P** — phenanthrene, **MP** — methylphenanthrenes, **Rc[%]** = 0.40 + 0.60(MPI1), **TrP1** — terphenyl ratio (Marynowski et al. 2001), **3-MeP/Ret** — 3-methylphenanthrene/retene ratio (Wilhelms et al. 1998)

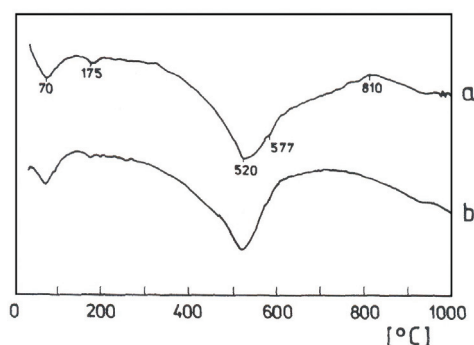


Fig. 2. DTA curves of the Triassic red clay of the Kozów deposit (sample 873) before (a) and after (b) removal of organic matter

In the group composition of extracts obtained from all the samples, the highest are the contents of aliphatic and polar fractions while those of aromatic fraction are low and very low (Table 1). The aromatic fractions contain aromatic hydrocarbons and some aromatic oxygen- and sulphur compounds.

MOLECULAR COMPOSITION OF ORGANIC MATTER

The commonly used parameter based on the distribution of *n*-alkanes, the Carbon Preference Index $CPI_{(25-31)}$, reaches values close to 1 for the samples from Chelsty and Kozów and a value above 1 for the Baranów sample (Table 1). In the latter case, the value indicates participation of higher plants in the formation of the organic matter. Relatively low $CPI_{(25-31)}$ values probably reflect very intense oxidation of organic matter. Oxidation, as with increase of thermal maturity, causes cracking of long-chain *n*-alkanes and the obliteration of differences between even and odd long-chain *n*-alkanes and results in the domination of shortchains.

The contribution of organic matter of terrestrial origin to the kerogene is confirmed by the presence of retene in all of the samples studied. As is widely known, the latter is an aromatic compound originating from resinous higher plants (e.g. Otto et al. 2002). The ratio of pristane to phytane (Pr/Ph) is commonly used in the reconstruction of redox conditions during deposition of organic matter (Peters, Moldowan 1993). However, the values ranging from 0.5 to 1.0 obtained for the clays studied are not diagnostic. As reported by Volkman and Maxwell (1986) and ten Haven et al. (1987), only values of Pr/Ph higher than 3.0 and lower than 0.5 definitively reflect oxic- and anoxic conditions, respectively.

The predominance of *n*-alkanes over isoprenoids, expressed by the indexes Pr/nC_{17} and Ph/nC_{18} (Table 1) and by the presence of hopanes, is indicative of the participation of organic matter of bacterial origin in the kerogene. Steranes, compounds originating from eucariotic organisms, do not occur or are only present in trace amounts. Their absence can be linked to the destructive effect of oxic conditions and to bacterial reworking of organic matter during early diagenesis; steranes are less resistant to such processes than are hopanes and isoprenoids.

Organic compounds identified in sedimentary organic matter are susceptible to decomposition and advanced destruction under oxic conditions. This is particularly evident from the distribution of aromatic and low-polar hydrocarbons such as benzo-phenone, fluorenone, cyclopenta(*def*)phenanthrenone (Fig. 3), anthracenone and benzanthrone (Fig. 4) in the material examined here. These hydrocarbons typically originate during strong oxidation and/or combustion of organic matter (Marynowski et al. 2004). The final stage of polycyclic aromatic hydrocarbon oxidation produces fatty acids (Anderson, Johns 1986); these, being very soluble in water, are prone to removal in migrating solutions. Polycyclic aromatic hydrocarbons such as naphthalene, biphenyl, phenanthrene, fluorene, fluoranthene, pyrene, chrysene and perylene, and especially their alkyl derivatives, are present in small amounts in the analysed material (Table 1). Moreover, unsubstituted polycyclic aromatic hydrocarbons predominate over their

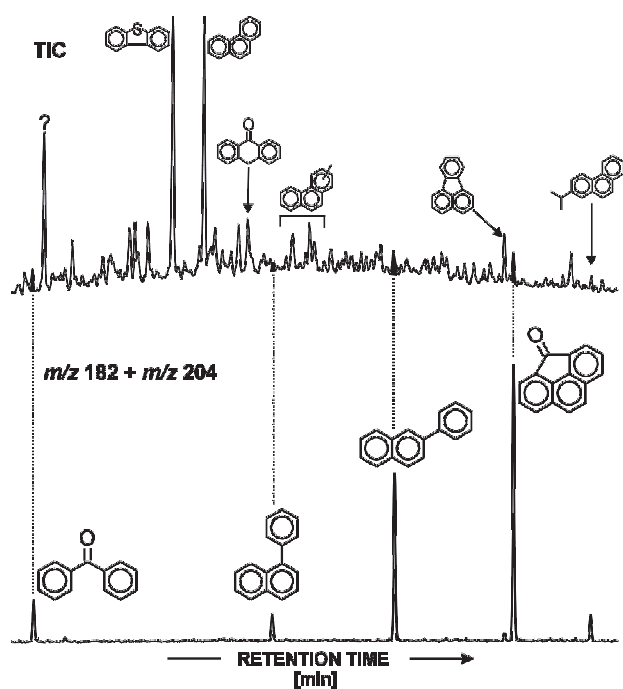


Fig. 3. Partial mass chromatogram showing distribution of benzophenone (m/z 182) and phenylnaphthalenes + cyclopenta(*def*)phenanthrene (m/z 204) in green clay from the Chelsty open pit (polar fraction). DB-5MS column was used

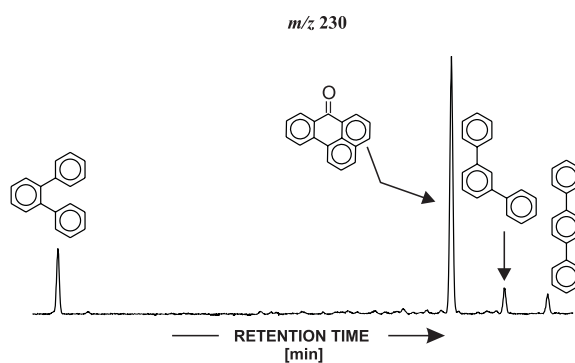


Fig. 4. Partial mass chromatogram showing distribution of terphenyls and benzanthrone (m/z 230) in green clay from the Chelsty open pit (polar fraction). DB-5MS column was used

methyl- derivatives. This is clearly shown on Figure 5 where phenanthrene is seen to dominate over 2-, 3-, 1- and 9-methylphenanthrenes. Such a distribution of aromatic compounds, characteristic of oxidized sedimentary organic matter (e.g. Sun, Püt-
tmann 2001), is probably a consequence of relatively fast conversion of the methyl-
and/or ethyl groups into aromatic aldehydes and ketones (see Wilkes et al. 1998).
According to Watson et al. (2005), oxygen compounds such as furans or xanthenes are

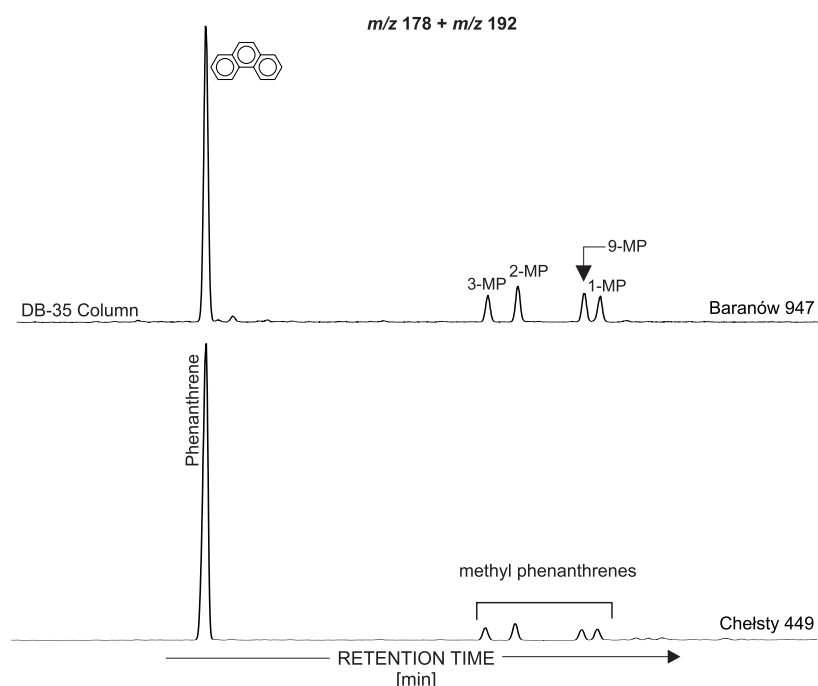


Fig. 5. Partial mass chromatograms showing distribution of phenanthrene and methyl phenanthrenes (m/z 178 + 192) in clays from Chelsty and Baranów open pits (aromatic fraction)

genetically associated with vascular plants, fungi and lichens. However, the majority of oxygen organic compounds described in this paper are typical of diagenetic transformations caused by abiotic oxidation of organic matter (see Charrié-Duhaut et al. 2000). Moreover, the red clays contain phenyl derivatives of aromatic compounds (PhPAC) such as phenylnaphthalenes (Fig. 3), terphenyls, phenyldibenzofurans and phenylphenanthrenes (Fig. 4). Their presence is not surprising as PhPAC originate during oxidation of organic matter — in many instances influenced by hydrothermal fluids (Marynowski et al. 2002a).

Other groups of organic compounds present in the clays include long-side chain alkylbenzenes, alkyltoluenes and branched long-side chain alkylbenzenes. Organic compounds of this type have been previously described in sedimentary organic matter (Fan et al. 1991; Ellis et al. 1996; Zhou et al. 2001). Their genesis, however, remains unclear (Sinninghe Damsté et al. 1988; Zhou et al. 2001).

The degree of organic matter maturity, based on the methylphenanthrene index and on the 3-methylphenanthrene/retene ratio (Table 1), is very similar in all of the clays examined and equates with that of Triassic carbonates (Marynowski et al. 2002b). Thermal maturity parameters for the clays, and for Triassic limestones and dolostones, are compared in Figure 1.

CONCLUSIONS

The oxidation of organic matter obliterates many of the diagnostic features that identify its source. Nevertheless, the domination of odd long-chain *n*-alkanes in the Baranów material and the presence of retene in all of the samples examined are indicative of higher plant input into the kerogen. Aliphatic hydrocarbons survived oxidation to a remarkably greater extent than did aromatic hydrocarbons (see Anderson, Johns 1986). The latter were, in large measure, oxidised into ketones and chinones and, finally, into fatty acids soluble in water. Generally, these processes lowered the organic matter content in the clays to less than 0.1 wt.%. It is important to note that a comparison of the bulk and molecular compositions of organic matter in the red clays and green lenses and intercalations reveals no significant differences.

Oxidation during sedimentation and during early diagenesis resulted in a huge decrease in the organic matter content of the Triassic clays. In ceramic raw materials, this decrease is especially advantageous in the context of fast firing technologies used in the production of ceramic tiles.

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**WSTĘPNE WYNIKI BADAŃ MATERII ORGANICZNEJ
Z TRIASOWYCH IŁÓW NW OBRZEŻENIA GÓR ŚWIĘTOKRZYSKICH**

Streszczenie

W pracy przeprowadzono ogólną i molekularną charakterystykę materii organicznej pochodzącej z triasowych iłów NW obrzeżenia Gór Świętokrzyskich. Badaniom poddano frakcje: apolarną, aromatyczną oraz polarną wykorzystując metodę chromatografii gazowej sprzężonej ze spektrometrią mas (GC-MS). Udział lądowych roślin wyższych w składzie kerogenu został stwierdzony na podstawie obecności wśród węglowodorów nasyconych wyraźnej przewagi długołańcuchowych, nieparzystowęglowych *n*-alkanów nad *n*-alkanami parzystowęglowymi. Ponadto, wszystkie badane próbki zawierają charakterystyczny dla roślin wyższych biomarker — reten. Frakcje polarne analizowanych próbek zawierają: benzofenon, fluorenon, cyklopenta(*def*)fenantrenon, antracenon i benzantron. Związki te powstają podczas intensywnego, abiotycznego utleniania materii organicznej. Z kolei we frakcji aromatycznej stwierdzono występowanie fenylowych pochodnych węglowodorów aromatycznych, takich jak: fenylo-naftaleny, terfenyle, fenylo-dibenzofurany i fenylofenantreny, również genetycznie związanych z procesami utleniania. Procesy abiotycznego utleniania materii organicznej zachodzące w trakcie jej depozycji i podczas wczesnej diagenety spowodowały znaczący spadek zawartości materii organicznej w iłach, co wpłynęło na ich właściwości technologiczne.